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(54) CURABLE PHOTOCHROMIC COMPOSITION

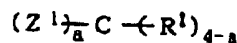
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(57) Abstract:

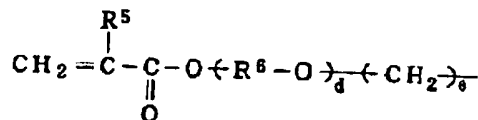
PROBLEM TO BE SOLVED: To obtain a curable photochromic compsn. which exhibits a high coloration density and a high fading rate and is suitable for ophthalmic lenses, by compounding a polymerizable tri- to hexafunctional (meth)acrylate monomer (e.g. trimethylolpropane trimethacrylate), optionally another acrylate monomer or a styryl monomer, and a photochromic compd.

SOLUTION: This compsn. is prepd. by compounding 100 pts.wt. monomer component comprising 10-100 pts.wt. polymerizable tri- to hexafunctional (meth) acrylate monomer, such as of formula I (wherein Z¹ is an org. group of formula II; R¹ is H or 1-4C alkyl; a is 3 or 4; R⁵ is H or CH₃; R⁶ is ethylene or propylene; d is 0-10; and e is 0 or 1), and 0-90 pts.wt. monomer selected from among polymerizable difunctional (meth)acrylate monomers, other polymerizable (meth)acrylate monomers, and polymerizable styryl monomers with 0.001-10 pts.wt. photochromic compd. Fulgide, and a spirooxazine compd. are suitable as the photochromic compd.

chromene⁸



I



II

(B) 5
TMPTMA
GMA 6
= cl. eth ac
(D) DVB 7
= cl. (C)

AN 1998:816652 CAPLUS
 DN 130:117398
 ED Entered STN: 01 Jan 1999
 TI Crosslinkable **photochromic** compositions with excellent coloring properties
 IN Hara, Tadashi; Tanizawa, Tsuneyoshi
 PA Tokuyama K. K., Japan
 SO Jpn. Kokai Tokkyo Koho, 13 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C09K009-02
 ICS C08F212-00; C08F220-28; C08F222-14
 CC 74-9 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)
 Section cross-reference(s): 38, 73

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PRAI JP 1997-152413		19970610		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 10338869	ICM	C09K009-02
	ICS	C08F212-00; C08F220-28; C08F222-14

AB **Photochromic** compns. are described which comprise 100 parts of a polymerizable monomer contg. (A) 10-100 parts of a tri- or hexa-functional (meth)acrylate monomer having a formula (Z1)aC(R1)4-a or (Z2)bC(R2)3-bR3C(R4)3-c(Z3)c [R1, 2, 4 = H, C1-4 alkyl; R3 = C1-4 alkylene, CH2OCH2; R5 = H, Me; R6 = Et, propylene; Z1-3 = CH2:CR5CO2(R6O)d(CH2)e; a = 3, 4; b, c = 0-3; b + c = 3-6; d = 0-10 integer; e = 0, 1] and 0-90 parts (B) a difunctional (meth)acrylate monomer CH2:CR7CO2(CR8HCH2O)f(CH2CR9HO)gCOCR10:CH2 [R7-10 = H, Me; f, g = 0-14 integer; f + g = 3-14], (C) a (meth)acrylate monomer (not A and B), or a styryl polymerizable monomer and 0.001-10 parts **photochromic** compds. A cured **photochromic** material, manufd. by curing the compn., is also claimed. The material shows high coloring concn., rapid discoloration rate, and small initial coloring property.

ST **photochromic** compn curing acrylate styryl copolymer

IT **Photochromic** materials

(crosslinkable **photochromic** compn. contg. acrylate-styryl copolymer)

IT 123803-85-0 124956-65-6 134167-18-3 139083-65-1,
 N-Cyanomethyl-6,7-dihydro-2-(p-methoxyphenyl)-4-methylspiro(5,6-benzo[b]thiophenedicarboxyimido-7,2-tricyclo[3.3.1.1]decane

139083-75-3,

N-Cyanomethyl-6,7-dihydro-4-methyl-2-phenylspiro(5,6-benzo[b]thiophenedicarboxyimido-7,2-tricyclo[3.3.1.1]decane 172971-94-7
 176028-40-3 176028-44-7 219655-86-4 219655-87-5

RL: DEV (Device component use); USES (Uses)

(crosslinkable **photochromic** compns. contg. acrylate-styryl copolymers)

IT 82727-34-2P 219655-69-3P 219655-70-6P 219655-71-7P
 219655-72-8P 219655-73-9P 219655-75-1P
 219655-76-2P 219655-78-4P 219655-80-8P 219655-81-9P
 219655-82-0P 219655-84-2P 219655-85-3P

RL: DEV (Device component use); IMF (Industrial manufacture); PREP

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The coloring concentration of this invention of a photochromic property is high, and its fading rate is quick, and, moreover, it relates to the suitable constituent for manufacture of the small photochromic hardening object of initial coloring.

[0002]

[Description of the Prior Art] Photochromism is a phenomenon which has pulled attention since the past several years, and when a color will change promptly if the light which includes ultraviolet rays like sunlight or the light of a mercury-vapor lamp in a certain compound is irradiated, the exposure of light is stopped and it puts on a dark place, it is the thing of the reversible operation which returns to the original color. Although the compound which has this property was called the photochromic compound and the compound of various structures has been compounded from the former, these photochromic compounds do not have the enough coloring concentration near a room temperature.

[0003] Moreover, it is a fulgide system photochromic compound as a photochromic compound with which coloring concentration has been improved. The SUPIRO oxazine system photochromic compound (it only abbreviates to a SUPIRO oxazine compound hereafter) (only hereafter abbreviated to a fulgide compound), the chromene system photochromic compound (it only abbreviates to a chromene compound hereafter), etc. are known variously (USP4882438, USP4960678, USP5130058, USP5106998, publication number No. 28154 [two to], JP,3-11074,A, WO 94/22854, WO 95/05371, USP4913544, EP0600669). Although these photochromic compounds show high coloring concentration near a room temperature, when ultraviolet rays are intercepted, its speed (it is hereafter called a fading rate) which returns to the original color is slow, and they cannot be satisfied. Furthermore, with the high SUPIRO oxazine compound and high chromene compound of coloring concentration, it has the trouble that coloring (it is hereafter called initial coloring) in the condition of not irradiating ultraviolet rays is large.

[0004] On the other hand, it is known that the effect of an additive will also receive a photochromic property in the polymerization nature monomer used as a matrix and a

polymerization catalyst pan, and the technique of solving the above-mentioned trouble of a photochromic compound by amelioration of a matrix is also proposed. For example, the proposal about the constituent which raised the fading rate is made by the USP No. 3627690 official report by adding the basic component or weak acidic component of a minute amount to a chromene compound. Moreover, the photochromic constituent which improved coloring concentration and a fading rate is shown in the photochromic compound by adding the metal salt of a carboxylic acid at JP,8-286317,A or JP,2-302754,A. Furthermore, by using a specific polymerization nature monomer for EP-No. 0227337 official report, the amount of the polymerization catalyst used is made to decrease, and the manufacture approach of the photochromic goods which control disassembly of a specific SUPIRO oxazine compound is proposed.

[0005] However, when the above-mentioned technique was applied to the system of the polymerization nature constituent currently used widely by the glass lens etc., for example, it became clear that there is a problem that sufficient effectiveness is not acquired or other physical properties fall.

[0006] Moreover, although it is known that the coloring concentration of a photochromic compound will become large if a monomer which cheats out of the glass transition temperature of a hardening object low in a hardenability constituent is added and the degree of hardness of a hardening object is made low, there is a problem in adopting this approach from the point of material strength in the application of a glass lens etc.

[0007]

[Problem(s) to be Solved by the Invention] while the purpose of this invention enlarges coloring concentration, the developing, i.e., photochromic property, of the new technique with which the fault of the above conventional techniques is compensated, -- in addition -- and it is proposing the photochromic hardenability constituent to which a fading rate's is made quick, initial coloring is small-*(ed), and the physical characteristic of a hardening object is moreover satisfied.

[0008]

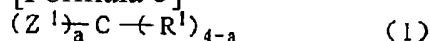
[Means for Solving the Problem] this invention persons continued research wholeheartedly about various hardenability constituents, in order to acquire the photochromic hardening object which has small initial coloring in big coloring concentration and a quick fading rate list and which is represented by the photochromic lens. Consequently, the photochromic hardenability constituent containing a specific polymerization nature monomer has the high coloring concentration of a photochromic property, and finds out a fading rate being not only quick, but giving the small photochromic hardening object of initial coloring moreover, and it came to complete this invention.

[0009] namely, the acrylate (meta) system polymerization nature monomer 10 of three organic functions this inventions are indicated to be by the [1] (i) (A) following general formula (1) or the general formula (3) thru/six organic functions - the 100 weight sections -- And (ii), (B): The acrylate (meta) system polymerization nature monomer of two organic functions shown by the following general formula (4), As opposed to the polymerization nature monomer 100 weight section which consists of a polymerization nature monomer 0 of acrylate (meta) system polymerization nature monomers other than

:the above (A) and (B), Or the (D):styryl system polymerization nature monomers which consists of a kind at least - the 90 weight sections (C) -- It is the photochromic hardenability constituent characterized by coming to carry out 0.001-10 weight section content of the [2] photochromic compounds.

[0010]

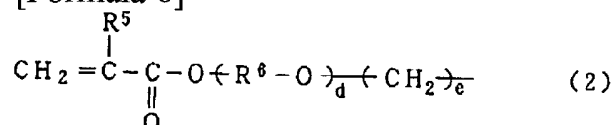
[Formula 5]



[0011] The inside of [type and Z1 are the following general formula (2).

[0012]

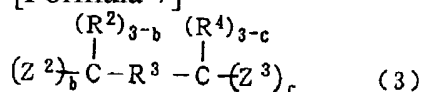
[Formula 6]



[0013] R5 is a hydrogen atom or a methyl group among {type, R6 is ethylene or a propylene radical, d is the integer of 0-10 (when d is 0, a mere joint hand is expressed.), and e is 0 or 1 (when e is 0, a mere joint hand is expressed.). It is the organic radical shown by}, R1 is the alkyl group of the carbon numbers 1-4 which may have the hydrogen atom or the substituent, and a is 3 or 4.]

[0014]

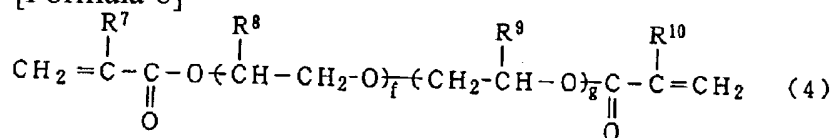
[Formula 7]



[0015] Z2 and Z3 are organic radicals shown by said general formula (2) which may differ mutually among {type, R2 and R4 are the alkyl groups of the carbon numbers 1-4 which may have the hydrogen atom or substituent which may be mutually different, R3 is the alkylene group of carbon numbers 1-4, or -CH2OCH2-, b and c are the integers of 0-3, respectively, and b+c is 3-6. }

[0016]

[Formula 8]



[0017] (R7, R8, R9, and R10 are the hydrogen atoms or methyl groups which may be different among a formula, respectively, f and g are the integers of 0-14, respectively, and f+g is 3-14.)

In the photochromic hardenability constituent of this invention, the hardening object which can be used suitable for the glass lens whose photochromic properties, such as coloring concentration, a fading rate, and initial coloring, improved can be given by blending the acrylate (meta) system polymerization nature monomer of three organic functions shown

by the (A):above-mentioned general formula (1) or (3) thru/or six organic functions.

[0018]

[Embodiment of the Invention] the photochromic hardenability constituent of this invention -- (i) and (A): -- below acrylate (meta) system polymerization nature monomer {of three organic functions shown by said general formula (1) or general formula (3) thru/or six organic functions } 10 only called (A) component - the 100 weight sections, and (ii), (B) : Below acrylate (meta) system polymerization nature monomer {of two organic functions shown by the following general formula (4) }, (C) which are also only called (B) component : Below acrylate (meta) system polymerization nature monomer {other than the above (A) and (B) } only called (C) component or (D): Use the polymerization nature monomer (only henceforth a polymerization nature monomer [1]) which consists of a polymerization nature monomer 0 of the styryl system polymerization nature monomers {it is also only hereafter called the (D) component} which consists of a kind at least - the 90 weight sections.

[0019] Especially limitation will not be carried out if the (A) component in a polymerization nature monomer [1] is an acrylate system polymerization nature monomer shown by said general formula (1) or (3) (meta). R1 in said general formula (1) is the alkyl group of the carbon numbers 1-4 which may have the hydrogen atom or the substituent here. The above-mentioned carbon number does not contain the carbon number in a substituent here (hereafter, when saying a carbon number about other radicals, the carbon number in a substituent is not included.). If this alkyl group is illustrated concretely, a methyl group, an ethyl group, a propyl group, butyl, an isopropyl group, t-butyl, etc. will be mentioned. Moreover, as a substituent which these alkyl groups may have, a well-known substituent is used that there is no limit in any way. If this substituent is illustrated concretely, alkoxy groups, such as halogen atoms, such as hydroxyl, a fluorine, chlorine, a bromine, and iodine, a methoxy group, an ethoxy radical, and a propoxy group, will be mentioned. Moreover, a in said general formula (1) is 3 or 4. When a is two or less, improvement in a photochromic property and the physical properties of a hardening object cannot be reconciled.

[0020] Moreover, Z1 in said general formula (1) is expressed with said general formula (2). R6 in a general formula (2) is ethylene or a propylene radical. Although R6 may be which [these] radical, in the viewpoint of ethylene being desirable and making initial coloring of a photochromic property small in the viewpoint of enlarging the degree of hardness of a hardening object, a propylene radical is desirable. Moreover, d is the integer of 0-10 (when d is 0, a mere joint hand is expressed). If d exceeds 10, the degree of hardness of a hardening object will become small, and the effectiveness of this invention will not fully be discovered. The still more desirable range of d is 0-6. Moreover, e is 0 or 1 (when e is 0, a mere joint hand is expressed). Since acquisition of a raw material becomes remarkably difficult when e is two or more, it is not realistic. Moreover, when the stability of this monomer is taken into consideration, as for e, it is desirable that it is 1.

[0021] In said general formula (3), Z2 and Z3 are independently synonymous with Z1 in said general formula (1) respectively, and they are expressed with a general formula (2). Again. R3 in a general formula (3) is the alkylene group of carbon numbers 1-4, or

-CH₂OCH₂-. Although a radical well-known as this alkylene group is used that there is no limit in any way, if this alkylene group is illustrated concretely, methylene group, ethylene, trimethylene radical, tetramethylen radical, dimethyl methylene group, 1, and 2-dimethyl ethylene etc. can be mentioned. Although R₃ may be any of an alkylene group and -CH₂OCH₂-, -CH₂OCH from ease of raw material acquisition²- is desirable.

[0022] Moreover, R₂ and R₄ in said general formula (3) are the alkyl group of the carbon numbers 1-4 which may have the hydrogen atom or substituent which may be mutually different. The thing same as an alkyl group of carbon numbers 1-4 as said R₁ which may have the substituent here is mentioned.

[0023] Moreover, b and c in said general formula (3) are the integer of 0-3, respectively, and b+c is 3-6. When b+c is smaller than 3, improvement in a photochromic property and the physical properties of a hardening object cannot be reconciled.

[0024] If the compound which can be suitably used as a (A) component in this invention is illustrated concretely 1) -- trimethylolpropanetrimethacrylate 2 -- 1, 1, and 1-tris (methacryloyloxy ethoxy methyl) propane 3 -- 1, 1, and 1-tris (methacryloyloxy ethoxy methyl)-2-hydroxy ethane 4 -- 1 and 1 -- 1-tris (methacryloyloxy ethoxy methyl)-2-methoxyethane 5 -- the 1, 1, and 1-tris (methacryloyloxy ethoxy methyl)-2-chloroethane 6 -- 1, 1, 1-tris [methacryloyl OKISHITORI (ethoxy) methyl] propane 7 1, 1 and 1, 1', and 1' -- 1'-hexa (methacryloyloxy ethoxy methyl) ethyl ether 8 hexa [1, 1, 1, 3, 3, and 3-] [methacryloyloxy nona (ethoxy) methyl] propane 9 -- 1, 1, and 1-tris (acryloyloxy ethoxy methyl) propane etc. It can mention.

[0025] the amount of the (A) component in the polymerization nature monomer [1] 100 weight section used in the photochromic hardenability constituent of this invention -- the 10 - 100 weight section -- suitable -- 10 - 90 weight section -- it is 20 - 80 weight section still more suitably. When the amount of the (A) component in the polymerization nature monomer [1] 100 weight section is under 10 weight sections, improvement in a photochromic property and coexistence of the physical properties of a hardening object become difficult. (A) Although a component is a component indispensable to improvement in a photochromic property and maintenance of the physical characteristic of a hardening object wanting to be compatible and the mechanism of action is not clear, if the (A) component is used, probably that to which the free volume of a matrix becomes large can be presumed. For this reason, it is thought that a photochromic compound can move comparatively freely in a matrix, coloring concentration becomes large, and the fading rate is quick.

[0026] Although it is discovered even if only the (A) component is used for the effectiveness of this invention as a polymerization nature monomer [1] In order to raise amelioration of the moldability of a constituent, and the physical characteristic and photochromic property of a hardening object acquired, the polymerization nature monomer which consists of at least one kind of the (B) component, the (C) component, or the (D) component may be added to the a maximum of 90 weight section into the polymerization nature monomer [1] 100 weight section.

[0027] Especially if the (B) component in a polymerization nature monomer [1] is an acrylate system polymerization nature monomer shown by said general formula (4) (meta),

it will not be limited. R7, R8, R9, and R10 in said general formula (4) are the hydrogen atom or methyl group which may be different here, respectively. R8 and R9 have a desirable methyl group in the viewpoint of a hydrogen atom being desirable and making initial coloring of a photochromic property small in the viewpoint of enlarging the degree of hardness of a hardening object.

[0028] In said general formula (4), $f+g$ is 3-14. When $f+g$ is larger than 14, the degree of hardness of a hardening object becomes small, and a hardening object becomes weak when smaller than 3. The more desirable range of $f+g$ is 4-9.

[0029] If the compound which can be suitably used as a (B) component in this invention is illustrated concretely, 1 triethylene-glycol dimethacrylate 2 tetraethylene-glycol dimethacrylate 3 nona ethylene glycol dimethacrylate 4 tetrapod deca ethylene glycol dimethacrylate 5 tripropylene-glycol dimethacrylate 6 tetrapropylene glycol dimethacrylate 7 nona propylene glycol dimethacrylate 8 nona ethylene glycol diacrylate etc. can be mentioned. spec. p. 22
(C)

[0030] The (B) component in the constituent of this invention is suitably used, in order to adjust the physical characteristic of a hardening object. That is, if there are many amounts of the (A) component in a polymerization nature monomer [1], a hardening object will tend to become hard, and a hardening object will tend to become soft if there are many amounts of the (B) component. Therefore, what is necessary is to respond in the hardness demanded for every application (to or softness), and just to determine the amount of the (B) component suitably in the range of 0 - 90 weight section to the polymerization nature monomer [1] 100 weight section. (B) The loadings with a suitable component are 0 - 70 weight section, and further 0 - 60 weight sections to the polymerization nature monomer [1] 100 weight section.

[0031] Moreover, by blending the (C) component with a polymerization nature monomer [1], endurance of a photochromic compound can be made high or the refractive index of a hardening object can be adjusted. (C) A component will not be limited especially if it is acrylate (meta) system polymerization nature monomers other than the (A) component and the (B) component. If the (C) component used suitably is illustrated, glycidyl (meta) acrylate, beta-methyl glycidyl (meta) acrylate, bisphenol A-monoglycidyl ether-methacrylate, 4-glycidyoxy butyl methacrylate, 3-(glycidyl-2-oxyethoxy)-2-hydroxypropyl methacrylate, 3-(glycidyoxy-1-isopropoxy)-2-hydroxypropyl acrylate, 3-(glycidyoxy-2-hydroxy propoxy)-2-hydroxypropyl acrylate, A methyl acrylate, an ethyl acrylate (meta), butyl acrylate (meta), (Meta) Isobornyl (meta) acrylate, acrylic-acid (meta) benzyl, Acrylic-acid phenyl, TORIBUROMO phenyl (meta) acrylate, (Meta) 2-hydroxyethyl (meta) acrylate, phenoxy ethyl (meta) acrylate, Phenoxy polyethylene-glycol (meta) acrylate, alkoxy polyethylene-glycol (meta) acrylate, Monofunctional (meta) acrylate system monomers, such as alkoxy polypropylene-glycol (meta) acrylate and TORIFURORO methyl (meta) acrylate; Polybutylene GURIKORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, neopentyl GURIKORUJI (meta) acrylate, The acrylic acid and methacrylic ester compound of a 2 and 2'-screw (4-methacryloyloxyethoxyphenyl) propane, The acrylic acid and methacrylic ester compound of a 2 and 2'-screw (4-methacryloyloxy poly ethoxy

phenyl) propane, The acrylic acid and methacrylic ester compound of a 2 and 2'-screw (4-methacryloyloxy propoxy phenyl) propane, The acrylic acid and methacrylic ester compound of a 2 and 2'-screw (4-methacryloyloxy poly propoxy phenyl) propane, The acrylic acid and methacrylic ester compound of a 2 and 2'-screw (3, 5-dibromo-4-methacryloyl oxyethoxy) propane, The acrylic acid and methacrylic ester compound of water addition bisphenol A ethyleneoxide or a propylene oxide addition product, Dimethylol tricyclo DEKANJI (meta) acrylate, dimethylol tricyclodecane poly ETOKISHIJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, The resultant of ethylene glycol or a polyethylene glycol, and glycidyl (meta) acrylate, The resultant of propylene glycol or a polypropylene glycol, and glycidyl (meta) acrylate, The bisphenol A ethyleneoxide, or a propylene oxide addition product and the resultant of glycidyl (meta) acrylate, Polyfunctional (meta) acrylate system monomers, such as water addition bisphenol A ethyleneoxide or a propylene oxide addition product, a resultant of glycidyl (meta) acrylate, and urethane acrylate, etc. are mentioned. What is necessary is for these (meta) acrylate system monomers to mix and use a kind or two sorts or more, and just to determine the compounding ratio according to the application to be used. Especially although it will not be limited especially if the loadings of the (C) component in the amount of heavy affinity single [1] 100 weight section are the range of 0 - 90 weight section, it is suitable to choose below 70 weight sections, so that it may become 0.1 - 60 weight section.

[0032] (D) A component serves to raise the moldability of the amount of heavy affinity single [1]. (D) Especially if a component is a styryl system polymerization nature monomer, it will not be limited. As a (D) component which can be used suitably, styrene, chloro styrene, alpha methyl styrene, an alpha-methyl-styrene dimer, vinyl naphthalene, isopropenyl naphthalene, bromostyrene, a divinylbenzene, etc. are mentioned. What is necessary is for these styryl system monomers to be able to mix and use a kind or two sorts or more, and just to determine the compounding ratio according to the application to be used. Especially although it will not be limited especially if the loadings of the (D) component in the amount of heavy affinity single [1] 100 weight section are the range of 0 - 90 weight section, it is suitable to choose below 70 weight sections, so that it may become 0.1 - 60 weight section.

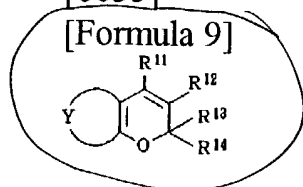
[0033] Next, the photochromic compound used in this invention is explained. The photochromic compound used by ** and this invention can adopt the compound in which a photochromic operation is shown that there is no limit in any way. For example, photochromic compounds, such as a fulgide compound, a chromene compound, and a SUPIRO oxazine compound, are known well, and these photochromic compounds can be used in this invention. As the above-mentioned photochromic compound, a well-known compound can be suitably used in USP4882438, USP4960678, USP5130058, USP5106998, WO 94/22854, WO 95/05371, USP4913544, and EP0600669 grade. What is necessary is for these photochromic compounds to be able to mix and use one sort or two sorts or more, and just to determine the compounding ratio according to the application to be used.

[0034] Among the above-mentioned photochromic compounds, compared with other

photochromic compounds, especially, since it is large, the improvement effectiveness of the photochromic property by this invention can use a chromene compound and a SUPIRO oxazine compound suitably. The chromene compound which can be suitably used in this invention can be expressed with a general formula (5).

[0035]

[Formula 9]



(5)

[0036] [-- however, that R11, R12, R13, and R14 are the same respectively or a different hydrogen atom, an alkyl group, an aryl group, the permutation amino group, a saturation heterocycle radical, or a partial saturation heterocycle radical -- it is -- R13 and R14 -- together -- becoming -- a ring -- forming -- **** [0037]

[Formula 10]



[0038] It comes out and the radical shown is the aromatic hydrocarbon radical or partial saturation heterocycle radical which may have the substituent, respectively.]

Among the above-mentioned formula (5), as an alkyl group shown by R11, R12, R13, and R14, the alkyl group of the carbon numbers 1-4, such as a methyl group and an ethyl group, can be mentioned, and the aryl group of the carbon numbers 6-10, such as a phenyl group, a tolyl group, a xylyl group, and a naphthyl group, can be mentioned as an aryl group. Moreover, the permutation amino group can mention the amino group by which at least one of the hydrogen atoms was permuted by an alkyl group or an aryl group which was described above, and a saturation heterocycle radical can mention the radical of the monovalence guided from five to 6 membered-ring which makes annular atoms nitrogen atoms, such as a pyrrolidine ring, an imidazolidine ring, a piperidine ring, a piperazine ring, and a morpholine ring, an oxygen atom, or a sulfur atom, and contains it 1-2 pieces. Moreover, as a partial saturation heterocycle radical, the radical of the carbon numbers 4-9 guided from a furan ring, a benzofuran ring, a thiophene ring, a benzothiophene ring, a pyrrole ring, the Indore ring, a pyridine ring, a quinoline ring, an isoquinoline ring, etc. can be mentioned.

[0039] The ring which R13 and R14 become together, and form can raise a NORUBORUNIRIDEN radical, a bicyclo [3.3.1] 9-Noni Liden radical, etc. among the above-mentioned formula (5).

[0040] Moreover, inside of the above-mentioned formula (5), [0041]

[Formula 11]



[0042] It comes out, and among the radicals of bivalence shown, as an aromatic hydrocarbon radical of bivalence, the radical of the bivalence guided from the one benzene ring or its 2-3 condensed ring can be mentioned, and the radical of the bivalence guided

from five to 7 membered-ring which makes annular atoms an oxygen atom, a nitrogen atom, or a sulfur atom, and contains it 1-2 pieces as a partial saturation heterocycle radical of bivalence, or the condensed ring of this and the benzene ring can be mentioned. If the radical of the carbon numbers 6-14 which will be guided from the benzene ring, a naphthalene ring, a phenanthrene ring, an anthracene ring, etc. if the aromatic hydrocarbon radical of bivalence is illustrated concretely can be raised and the partial saturation heterocycle radical of bivalence is illustrated concretely, the radical of the carbon numbers 4-9 guided from a furan ring, a benzofuran ring, a pyridine ring, a quinoline ring, an isoquinoline ring, a pyrrole ring, a thiophene ring, a thiophene ring, a benzothiophene ring, etc. can be mentioned.

[0043] Although not restricted, especially as these substituents, for example Chlorine, a bromine, Halogen atoms, such as iodine : The alkyl group: methoxy group of the carbon numbers 1-10, such as a methyl group and an ethyl group, The alkoxy group of the carbon numbers 1-10, such as an ethoxy radical : A phenyl group, a tolyl group, aryl group [of the carbon numbers 6-10, such as a xylyl group,]: -- alkoxy aryl group [of carbon numbers 7-14] (aryl group of carbon numbers 6-10 permuted by alkoxy group of carbon numbers 1-4): -- a piperidino radical -- The permutation amino-group:nitro group of the carbon numbers 1-10, such as a morpholino radical, the India Reno radical, and a dimethylamino radical,: A cyano group etc. can be illustrated.

[0044] Especially as [both] a chromene compound shown by said general formula (5), R11 and R12 are hydrogen atoms, and R13 and R14 are respectively the same, a bicyclo in which it is different aryl group, or is partial saturation heterocycle radical, or these were formed by becoming together [3.3.1] 9-Noni Liden radical, or a NORUBORUNIRIDEN radical, [0045]

[Formula 12]

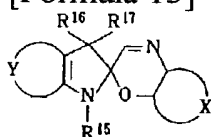


[0046] The compound which is the radical guided from the naphthalene ring which may be permuted by the alkyl group of ** and carbon numbers 1-10, the alkoxy group of carbon numbers 1-10, or the permutation amino group of carbon numbers 1-10 can use it suitably.

[0047] Moreover, the SUPIRO oxazine compound suitably used by this invention can be expressed with a general formula (6).

[0048]

[Formula 13]



(6)

[0049] It sets to a general formula (6) here. R15, R16, and R17 Respectively the same or a different alkyl group, a cycloalkyl radical, a cyclo aralkyl radical, An alkoxy group, an alkyleneoxy alkyl group, an alkoxy carbonyl group, An alkoxy carbonyl alkyl group, an aryl group, an aralkyl radical, an aryloxy radical, They are an alkylene thio alkyl group, an

acyl group, an acyloxy radical, or an amino group. R16 and R17 It may become together and a ring may be formed, R15, R16, and R17 may have a substituent, and a halogen atom, a nitro group, a cyano group, or a heterocycle radical is raised other than the above radicals as a substituent. moreover [0050]

[Formula 14]



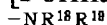
[0051] It comes out and the radical shown is the aromatic hydrocarbon radical or partial saturation heterocycle radical which may be permuted, respectively, [0052]

[Formula 15]



[0053] It comes out and the radical shown is the aromatic hydrocarbon radical or partial saturation heterocycle radical which may be permuted, respectively. Although the same radical as the substituent stated by above R15, R16, and R17 as a substituent can be chosen, it is especially. [0054]

[Formula 16]

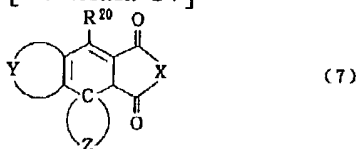


[0055] (-- however, R18 and R19 are alkyl groups, alkoxy groups, or allyl groups etc. which may be permuted, and R18 and R19 may be combined and cyclized mutually, and may form nitrogen-containing heterocycle.) -- the radical shown is suitable in the early photochromic engine performance at the point that the coloring concentration is high.

[0056] Moreover, an improvement operation of the photochromic property in this invention is discovered also to a fulgide compound. The fulgide compound used by this invention is expressed with a general formula (7).

[0057]

[Formula 17]



[0058] [-- however [0059]

[Formula 18]



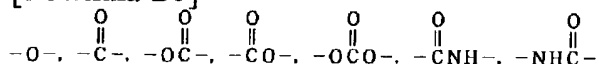
[0060] It is the aromatic hydrocarbon radical of the bivalence which may have the ***** substituent, or the partial saturation heterocycle radical of bivalence, and R20 is an alkyl group, an aryl group, or the heterocycle radical of monovalence, [0061]

[Formula 19]



[0062] They are **, a NORUBORUNIRIDEN radical, or an ADAMAN dust DIN radical. X An oxygen atom, radical >N-R21, radical >N-A1-B1-(A2) m-(B-2) n-R22, radical >N-A3-A4 or radical It is >N-A3-R23 (here), R21 is a hydrogen atom, an alkyl group, or an aryl group. A1, A2, and A3 it is the same or the alkylene group which may differ, an alkylidene radical, a cyclo alkylene group, or an alkyl cycloalkane-diyl radical, and B1 and B-2 are the same -- or you may differ [0063]

[Formula 20]



[0064] It is the radical of *****, and although m and n show 0 or 1 independently, respectively, when m is 0, n is 0, R22 is an alkyl group, a naphthyl group, or a naphthyl alkyl group, A4 is a naphthyl group and R23 is a halogen atom, a cyano group, or a nitro group.]

Inside of the above-mentioned formula (7), [0065]

[Formula 21]



[0066] Come out and the aromatic hydrocarbon radical or partial saturation heterocycle radical shown Although it is the same as that of the radical in said formula (5) and especially the substituent of each of these radicals is not restricted For example, the alkyl group of the carbon numbers 1-20, such as halogen atom:methyl groups, such as chlorine, a bromine, and iodine, and an ethyl group : A methoxy group, The alkoxy group of the carbon numbers 1-20, such as an ethoxy radical,: The aryl group:amino-group:nitro group:cyano group of the carbon numbers 6-10, such as a phenyl group, a tolyl group, and a xylyl group, etc. can be illustrated.

[0067] The alkyl group, aryl group, and heterocycle radical which are shown by R20 can mention the radical of the monovalence guided from 5 which makes annular atoms the alkyl group of the above-mentioned carbon numbers 1-4, the aryl group of carbon numbers 6-10 and an oxygen atom, a nitrogen atom, or a sulfur atom, and contains it 1-2 pieces - 7 membered-ring, or the condensed ring of this and the benzene ring among the above-mentioned formula (7).

[0068] The alkyl group and aryl group which are shown by R21 are the same as that of the above R20 among the above-mentioned formula (7). As for the alkylene group shown by A1, A2, and A3, it is desirable that it is the radical of the carbon numbers 1-4, such as a methylene group, ethylene, a propylene radical, a trimethylene radical, and a tetramethylen radical, and, as for an alkylidene radical, it is desirable that it is the radical of the carbon numbers 2-4, such as an ethylidene radical, a propylidene radical, and an isopropylidene radical, and a cyclo alkylene group has a desirable cyclo hexylene radical, and an alkyl cycloalkane-diyl radical has a still more desirable dimethylcyclohexane-diyl radical.

[0069] Moreover, the alkyl group shown by R22 is the same as that of the above R20 among the above-mentioned formula (7), and, as for a naphthyl alkyl group, it is desirable

that it is the radical of the carbon numbers 11-14, such as a naphthyl methyl group and a naphthyl ethyl group.

[0070] Also in the fulgide compound shown by the above-mentioned formula, when the endurance of a photochromic operation etc. is taken into consideration, R20 is an alkyl group, X is >N-R and R is the cyano alkyl group of carbon numbers 1-4, the nitro alkyl group of carbon numbers 1-4, or the alkoxy carbonyl alkyl group (the alkoxy group of carbon numbers 1-4 and the alkylene group of carbon numbers 1-4 are included) of carbon numbers 3-9, [0071]

[Formula 22]



[0072] It is a ** ADAMAN dust DIN radical, [0073]

[Formula 23]



[0074] The compound which are the heterocycle radical which may be permuted by **, the aryl group of carbon numbers 6-10, or the alkoxy aryl group (aryl group of the carbon numbers 6-10 permuted by the alkoxy group of carbon numbers 1-4) of carbon numbers 7-14, especially the radical guided from a thiophene ring is desirable.

[0075] When using the hardenability constituent in this invention for a glass lens, the color tone of gray or Brown is liked, but since such a color tone is not acquired with a single photochromic compound, the approach of mixing two or more sorts of different photochromic compounds is adopted. Although the above-mentioned fulgide compound and the above-mentioned SUPIRO oxazine compound generally color in a sour orange - blue, neutral colors, such as gray and Brown, can be obtained by mixing the chromene compound which colors to yellow - a sour orange at this.

[0076] The following compounds can be illustrated if the chromene compound, SUPIRO oxazine compound, and fulgide compound which can be suitably used as a photochromic compound in this invention are shown concretely.

[0077] Chromene compound: 1 spiro [norbornane -2, 2'-[2H] benzo [h] chromene]

2) The spiro [bicyclo [3.3.1] nonane -9, 2'-[2H] benzo [h] chromene]

3) The 7'-methoxy SUPIRO [bicyclo [3.3.1] nonane -9, 2'-[2H] benzo [h] chromene]

4) 7'-methoxy SUPIRO [norbornane -2, 2'-[2H] benzo [h] chromene]

5) 3 and 3-screw (3-fluoro-4-methoxypheny)-6-morpholino-3H-[benzo f] chromene 63, 3-screw (4-methoxypheny)-6-morpholino-3H-[benzo f] chromene

73-(3-trifluoromethyl-4-methoxypheny)-3- (4-methoxypheny)-6-thio

morpholino-3H-[benzo f] chromene SUPIRO oxazine compound: 11 '- methoxy

carbonylmethyl -8' '- methoxy-6''-(4-methyl piperazino) JISUPIRO () [a cyclohexane -1,]

[3' -] (3H) Indore-2' - (1'H), 3''-(3H) naphth (3, 2-a) (1 4) oxazine

2) 6'-fluoro - 1' and 5'- dimethyl-6''-morpholino JISUPIRO (a cyclohexane -1, 3'-(3H)

Indore-2' - (1'H), 3''-(3H) naphth (3, 2-a) (1 4) oxazine)

3) 6' - fluoro -5'-methyl-1' - isobutyl-6''-morpholino JISUPIRO (a cyclohexane -1, 3'-(3H)

Indore-2' - (1'H), 3''-(3H) naphth (3, 2-a) (1 4) oxazine)

4) 3' and 3' - dimethyl-1' - isopropyl -6' - India Reno spiro-(3H) Indore -2' - (1'H) -- 3''-(3H) naphth (3, 2-a) (1 4) oxazine 53', 3'-dimethyl-1' - isobutyl SUPIRO-(3H) Indore -2' - (1'H), 3''-(3H) naphth (3, 2-a) (1 4) oxazine fulgide compound: 1N-cyano methyl -6 and 7-dihydro-4-methyl-2-phenyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

2) N-cyano methyl -6, 7-dihydro-2-(p-methoxyphenyl)-4-methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

3) N-cyano methyl -6, 7-dihydro-4-methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

4) 6 7-dihydro-N-methoxy carbonylmethyl-4-methyl-2-phenyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

5) 6 7-dihydro-4-methyl-2-(p-methylphenyl)-N-nitro methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

6) N-cyano methyl -6, 7-dihydro-4-cyclo propyl-3-methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

7) N-cyano methyl -6, 7-dihydro-4-cyclo propyl-spiro (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

The loadings of the photochromic compound in the photochromic hardenability constituent of this invention are the range of 0.001 - 10 weight section to the polymerization nature monomer [1] 100 weight section. When the loadings of the photochromic compound to the polymerization nature monomer [1] 100 weight section are under the 0.001 weight section, the reversible endurance of a photochromic property is spoiled and 10 weight sections are exceeded, initial coloring of a hardening object becomes large. The suitable loadings of the photochromic compound for obtaining the good photochromic engine performance are the range of 0.01 - 5 weight section, especially 0.01 - 1 weight section to the polymerization nature monomer [1] 100 weight section.

[0078] Various stabilizers, such as a release agent, an ultraviolet ray absorbent, an infrared absorption agent, UV stabilizer, an antioxidant, a coloring inhibitor, an antistatic agent, fluorescent dye, a color, a pigment, and perfume, and an additive can be further mixed and used for the photochromic hardenability constituent of this invention if needed.

[0079] Since the endurance of a photochromic compound can be further raised if the above-mentioned UV stabilizer is mixed and used, it is suitable. Since especially a fulgide compound has the large effectiveness of the improvement in endurance by UV stabilizer, when mixing and using a fulgide compound and a chromene compound which were described above, it can prevent a change of the neutral colors of these compounds with time good.

[0080] As UV stabilizer, hindered amine light stabilizer, hindered phenol light stabilizer, and a sulfur system antioxidant can be used suitably.

[0081] Although especially the amount of the UV stabilizer used is not restricted, it is usually suitable that the loadings of each UV stabilizer are the range of 0.001 - 10 weight section, and further 0.01 - 1 weight section to the polymerization nature monomer [1] 100 weight section.

[0082] Furthermore, when using a fulgide compound and a chromene compound together, a change of the mixed color of these photograph clo compounds with time can be suppressed by adding a phosphite compound. Therefore, it is most suitable in this invention to use both of the UV stabilizer and the phosphite compound which were described above in the system which uses a fulgide compound and a chromene compound together. As for the loadings of a phosphite compound, it is desirable that they are 0.001 - 10 weight section, and further 0.01 - 1 weight section to the polymerization nature monomer [1] 100 weight section.

[0083] Furthermore, if an infrared absorption agent is mixed and used, the photochromic hardening object which also has infrared absorption ability besides a photochromic operation can be acquired again. Although a poly methine system compound, a G MONIUMU system compound, a cyanine system compound, an anthraquinone system compound, and an aluminum system compound can be used as an infrared absorption agent, a molecular extinction coefficient is large and the G MONIUMU system compound which demonstrates effectiveness by addition of a small amount is suitable.

[0084] As for the loadings of an infrared absorption agent, it is desirable that they are 0.0001 - 1 weight section, and further 0.001 - the 0.01 weight sections to the polymerization nature monomer [1] 100 weight section.

[0085] Especially the polymerization method that acquires a hardening object from the photochromic constituent of this invention is not restrictive, and can adopt the well-known radical polymerization approach. The exposure of use of radical polymerization initiators, such as various peroxides and an azo compound, or ultraviolet rays, alpha rays, beta rays, a gamma ray, etc. or both concomitant use can perform a polymerization initiation means. If a typical polymerization method is illustrated, after pouring in the photochromic constituent of this invention which mixed the radical polymerization initiator and making it oxidize all over an air furnace between the mold currently held with the elastomer gasket or the spacer, the casting polymerization to remove is adopted.

[0086] Although it is not limited especially as a radical polymerization initiator but a well-known thing can be used. When a typical thing is illustrated, benzoyl peroxide, p-chlorobenzoyl peroxide, Diacyl peroxide, such as decanoyl peroxide, lauroyl peroxide, and acetyl peroxide; Tert-butyl peroxide-2-ethyl hexoate, T-butyl peroxy neodecanate, cumyl peroxy neodecanate, Peroxy ester, such as t-butyl peroxybenzoate; azo compounds [, such as par carbonate; azobisisobutyronitril,], such as diisopropyl peroxy dicarbonate and di-sec-butyl peroxydicarbonate, etc. can be raised.

[0087] although the amount of the radical polymerization initiator used changes with presentations of polymerization conditions, the class of initiator, and the aforementioned monomer and it cannot generally limit -- general -- the polymerization nature monomer [1] 100 weight section -- receiving -- 0.001 - 10 weight section -- the range of 0.01 - 5 weight section is preferably suitable.

[0088] Especially temperature affects the description of the photochromic hardening object acquired among polymerization conditions. Although limitation is impossible generally since this temperature condition is influenced according to the class of initiator, and the class of an amount or monomer, it is suitable to perform the so-called taper type which

generally starts a polymerization at low temperature comparatively, raises temperature slowly, and is stiffened under an elevated temperature at the time of polymerization termination of two-step polymerization. Although it is suitable to decide on the optimal time amount according to these conditions beforehand since it changes with various kinds of factors like [polymerization time amount] temperature, it is desirable to choose conditions so that a polymerization may generally be completed in 2 - 40 hours.

[0089] Furthermore, the photochromic hardening object acquired by the above-mentioned approach can also perform the following processings according to the application. That is, it is also possible to perform processing and secondary treatment of the acid-resisting processing by the rebound ace court agent which uses sols, such as dyeing, the silane coupling agent and silicon using colors, such as a disperse dye, a zirconium, antimony, aluminum, tin, and a tungsten, as a principal component, vacuum evaporation of the thin film of the metallic oxide of SiO₂, TiO₂, and ZrO₂ grade, or spreading of the thin film of an organic macromolecule, antistatic treatment, etc.

[0090]

[Effect of the Invention] The hardening object acquired by carrying out the polymerization of the photochromic hardenability constituent of this invention is not only excellent in the coloring concentration of a photochromic property, a fading rate, and initial coloring but excellent in physical properties, such as a degree of hardness of a hardening object. The photochromic hardening object which was furthermore excellent in transparency, solvent resistance, thermal resistance, shock resistance, coat nature, and a dye affinity can be acquired.

[0091] Therefore, the hardening object acquired by carrying out the polymerization of the photochromic constituent of this invention can be used suitable for the application of a photochromic lens etc. useful as organic glass which has photochromic nature.

[0092]

[Example] Although an example is hereafter hung up and explained in order to explain this invention concretely, this invention is not limited to these examples.

[0093] (A) - (D) component and the photochromic compound which were used in the following examples are the following compound.

[0094] (A) Three organic functions of a component or Six organic functions Acrylate system monomer : (Meta) TMPT:trimethylolpropanetrimethacrylate TMEP: -- 1, 1, and 1-tris (methacryloyloxy ethoxy methyl) propane TEOE: -- 1, 1, and 1-tris (methacryloyloxy ethoxy methyl)-2-hydroxy ethane TECE: -- 1 and 1 -- 1-tris (-- methacryloyloxy one -- ethoxy -- methyl --) - two - chloroethane -- TMTP -- : -- one -- one -- one - tris -- [-- methacryloyl one -- OKISHITORI (ethoxy) -- methyl --] -- a propane -- HMEE -- : -- one -- one -- one -- one -- ' -- one -- ' -- one -- ' - hexa (methacryloyloxy ethoxy methyl) -- ethyl ether -- (B) -- 2 organic-functions (meta) acrylate system monomer [of a component]: -- 3PG:tripropylene glycol dimethacrylate 4PG:tetrapropylene glycol dimethacrylate (with the mixture of polypropylene-glycol dimethacrylate) The monomer whose number of average mols of an oxypropylene chain is 4 9PGes: Nona propylene glycol dimethacrylate (monomer whose number of average mols of an oxypropylene chain is 9 with the mixture of polypropylene-glycol dimethacrylate)

4G: Tetraethylene glycol dimethacrylate (monomer whose number of average mols of an oxyethylene chain is 4 with the mixture of polyethylene glycol dimethacrylate)

(C) The styryl system monomer MS:alpha-methyl-styrene DMS:alpha-methyl-styrene dimer photochromic compound of acrylate (meta) system monomer GMA:glycidyl methacrylate HEMA:propane [2-hydroxyethyl methacrylate BPE:2 and 2-screw

(methacryloyloxyethoxyphenyl)] (D) component of a component : chromene compound; c1: The spiro [bicyclo [3.3.1] nonane -9, 2'-[2H] benzo [h] chromene]

The c2:7'-methoxy SUPIRO [bicyclo [3.3.1] nonane -9, 2'-[2H] benzo [h] chromene]

c -- three -- : -- three -- three - a screw (3-fluoro-4-methoxypheny) - six - morpholino - [-- three -- H --] -- benzo -- [-- f --] -- a chromene -- c -- four -- : -- three -- three - a screw (4-methoxypheny) - six - morpholino - [-- three -- H --] -- benzo -- [-- f --] -- a chromene -- SUPIRO -- oxazine -- a compound --;

s1:6'-fluoro - 1' and 5'- dimethyl-6"-morpholino JISUPIRO (a cyclohexane -1, 3'-(3H)

Indore-2'- (1'H), 3"-(3H) naphth (3, 2-a) (1 4) oxazine)

s2:6' - fluoro -5'-methyl-1'- isobutyl-6"-morpholino JISUPIRO (a cyclohexane -1, 3'-(3H)

Indore-2'- (1'H), 3"-(3H) naphth (3, 2-a) (1 4) oxazine)

s3:3', 3'-dimethyl - 1' - Isobutyl SUPIRO-(3H) Indore-2'- (1'H), 3"-(3H) naphth (3, 2-a) (1 4) oxazine fulgide compound;

f1: N-cyano methyl -6 and 7-dihydro-4-methyl-2-phenyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

f2: N-cyano methyl -6, 7-dihydro-2-(p-methoxypheny)-4-methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

f3: N-cyano methyl -6, 7-dihydro-4-methyl SUPIRO (5 and 6-benzo [b] thiophenedicarboxyimide -7, 2-tricyclo [3.3.1.1] Deccan)

To the constituent which consists of (A) - (D) component and the photochromic compound which were shown in one to examples 1-17 and example of comparison 3 table 1, 1 weight section addition of the tert-butyl peroxide-2-ethyl hexoate could be carried out as a radical polymerization initiator, and it mixed. This mixed liquor was poured in into the mold which consisted of gaskets which consist of a glass plate and an ethylene-vinylacetate copolymer, and the casting polymerization was performed. Using the air furnace, a polymerization is applied at 30 to 90 degrees C for 18 hours, raises temperature gradually, and held it at 90 degrees C for 2 hours. Mold was removed from the air furnace after polymerization termination, and the hardening object was removed from the glass mold of mold after radiationnal cooling.

[0095]

[Table 1]

表 1

No.	フォトクロミック組成物の配合比 (重量部)				
	A) 3～6官能 (メタ)アクリレート	B) 2官能 (メタ)アクリレート	C) (メタ)アクリル系 単量体	D) スチレン系 単量体	フォトクロミック 化合物
1	TMTP: 100	—	—	—	c 4 : 0. 05
2	TMEP: 70	—	GMA: 20	DMS: 1	s 1 : 0. 05
3	TMPT: 35	9PG: 55	GMA: 8	DMS: 1	c 1 : 0. 05
4	TMPT: 40	9PG: 50	—	DMS: 1	c 2 : 0. 05
5	TMEP: 50	9PG: 40	GMA: 9	DMS: 1	c 3 : 0. 05
6	TMEP: 30	4PG: 60	GMA: 9	DMS: 1	c 4 : 0. 05
7	TMEP: 30	4G: 60	GMA: 9	DMS: 1	s 1 : 0. 05
8	HMEE: 40	9PG: 50	GMA: 9	DMS: 1	s 2 : 0. 05
9	TMPT: 15	4PG: 35	GMA: 9 BPE: 40	DMS: 1	s 3 : 0. 05
10	TECE: 70	14G: 20	GMA: 8	DMS: 1	f 1 : 0. 05
11	TEOE: 50	9PG: 40	GMA: 8	DMS: 1	f 2 : 0. 05
12	HMEE: 30	9G: 60	GMA: 10	—	f 3 : 0. 05

[0096]

[Table 2]

表 1 (続き)

No.	フォトクロミック組成物の配合比 (重量部)				
	A) 3～6官能 (メタ)アクリレート	B) 2官能 (メタ)アクリレート	C) (メタ)アクリル系 単量体	D) スチレン系 単量体	フォトクロミック 化合物
13	TMPT: 85	9PG: 55	GMA: 5 HEMA: 4	DMS: 1	c 1 : 0. 05 f 2 : 0. 10
14	TMEP: 50	9PG: 40	GMA: 8	DMS: 1	c 2 : 0. 09 f 1 : 0. 13
15	TMEP: 30	4PG: 40	GMA: 8 BPE: 20	DMS: 1	c 4 : 0. 05 s 1 : 0. 15
16	TMTP: 60	3PG: 30	GMA: 5	MS: 4 DMS: 1	c 3 : 0. 05 f 2 : 0. 10 s 1 : 0. 05
17	HMEE: 40	9PG: 50	GMA: 9	DMS: 1	c 2 : 0. 05 c 3 : 0. 04 f 2 : 0. 10 s 2 : 0. 05
比較例 1	—	3PG: 80	GMA: 8	DMS: 1	c 1 : 0. 05
比較例 2	—	9PG: 80	GMA: 8	DMS: 1	s 1 : 0. 05
比較例 3	—	—	GMA: 8 BPE: 90	DMS: 1	c 4 : 0. 05

[0097] ***** of the photochromic property of the acquired photochromic hardening object and a hardening object was examined by the following approaches.

[0098] (1) irradiate Hamamatsu Photonics 100 [xenon lamp L-2480(300W) SHL-] for 120 seconds, the coloring color tone and the coloring concentration profit **** photochromic hardening object (thickness of 2mm) were made to color them through an aero mass filter (Corning, Inc. make) by beam on-the-strength [of 365nm] =2.4mW[/cm]2,245nm=24 microwatt/cm 2 in 20-degree-C **1 degree C and a photochromic hardening body surface, and the coloring color tone was judged visually. Moreover, the value of epsilon(120 seconds)-epsilon (0 second) was calculated, and it considered as coloring concentration. However, epsilon (120 seconds) is an absorbance after for [of a under / the above-mentioned conditions of the photochromic hardening object in the maximum absorption wavelength / optical exposure] 120 seconds, and epsilon (0 second) is the absorbance of the non-radiation-hardening object in the maximum absorption wavelength at the time of an optical exposure.

[0099] (2) It expressed with time amount t1/2 taken for the coloring concentration for

which it asked at the fading rate (1) to fall to 1/2.

[0100] (3) It expressed with the absorbance in the maximum absorption wavelength in the condition of not irradiating an initial coloring xenon lamp.

[0101] (4) The value in L-scale was measured about the hardening object with a thickness of 2mm using the surface hardness Rockwell hardness meter.

[0102] The physical-properties evaluation result of each hardening object was shown in Table 2.

[0103]

[Table 3]

表 2

No.	発色色調	発色濃度	t _{1/2} (分)	初期着色	表面硬度
1	黄色	1. 8	1. 5	0. 0 5	1 1 2
2	赤紫色	1. 4	0. 6	0. 0 1	1 1 6
3	黄色	1. 4	8. 6	0. 0 1 >	9 7
4	橙色	1. 4	8. 4	0. 0 1 >	9 9
5	黄色	1. 7	2. 4	0. 0 2	1 0 0
6	黄色	1. 8	1. 6	0. 0 5	1 0 2
7	赤紫色	1. 5	0. 6	0. 0 1	1 0 4
8	青紫色	1. 7	0. 4	0. 0 3	9 9
9	青色	0. 7	0. 1	0. 0 1 >	9 8
1 0	赤紫色	0. 9	0. 9	0. 0 1 >	9 6
1 1	青紫色	1. 0	1. 0	0. 0 1 >	1 0 0
1 2	赤紫色	0. 7	0. 5	0. 0 1 >	9 4

[0104]

[Table 4]

表 2 (続き)

No.	発色色調	発色濃度	t _{1/2} (分)	初期着色	表面硬度
1 3	グレー	1. 0	1. 8	0. 0 1 >	9 7
1 4	ブラウン	1. 1	4. 5	0. 0 1 >	1 0 0
1 5	グレー	1. 0	1. 3	0. 0 3	1 0 3
1 6	グレー	1. 0	1. 2	0. 0 2	1 0 0
1 7	ブラウン	1. 1	8. 9	0. 0 2	9 7
比較例 1	黄色	1. 0	9. 8	0. 0 1 >	1 0 2
比較例 2	赤紫色	1. 4	0. 6	0. 0 1	5 0 以下 (測定不能)
比較例 3	黄色	1. 1	2. 9	0. 1 0	1 1 0

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

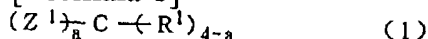
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

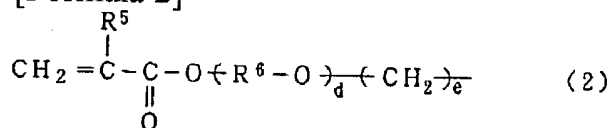
[Claim 1] [1 (i)], (A) : The acrylate (meta) system polymerization nature monomer 10 of three organic functions shown by the following general formula (1) or the general formula (3) thru/or six organic functions - the 100 weight sections, And (ii), (B) : The acrylate (meta) system polymerization nature monomer of two organic functions shown by the following general formula (4), As opposed to the polymerization nature monomer 100 weight section which consists of a polymerization nature monomer 0 of the amounts of acrylate (meta) system pile affinity single other than :the above (A) and (B), or the (D):styryl system polymerization nature monomers which consists of a kind at least - the 90 weight sections (C) -- The photochromic hardenability constituent characterized by coming to carry out 0.001-10 weight section content of the [2] photochromic compounds.

[Formula 1]



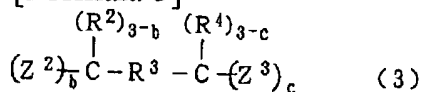
The inside of [type and Z1 are the following general formula (2).

[Formula 2]



R5 is a hydrogen atom or a methyl group among {type, R6 is ethylene or a propylene radical, d is the integer of 0-10 (when d is 0, a mere joint hand is expressed.), and e is 0 or 1 (when e is 0, a mere joint hand is expressed.). It is the organic radical shown by}, R1 is the alkyl group of the carbon numbers 1-4 which may have the hydrogen atom or the substituent, and a is 3 or 4.]

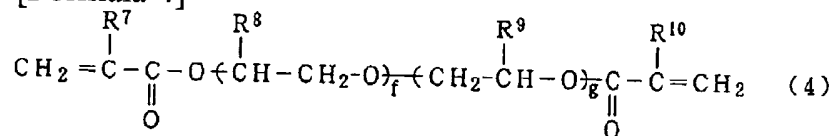
[Formula 3]



Z2 and Z3 are organic radicals shown by said general formula (2) which may differ

mutually among {type, R2 and R4 are the alkyl groups of the carbon numbers 1-4 which may have the hydrogen atom or substituent which may be mutually different, R3 is the alkylene group of carbon numbers 1-4, or -CH₂OCH₂-, b and c are the integers of 0-3, respectively, and b+c is 3-6. }

[Formula 4]



(R7, R8, R9, and R10 are the hydrogen atoms or methyl groups which may be different among a formula, respectively, f and g are the integers of 0-14, respectively, and f+g is 3-14.)

[Claim 2] The photochromic nature hardening object which makes it come to harden a photochromic hardenability constituent according to claim 1.

[Translation done.]